

Tanaka et al

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TITLE: POLISHING COMPOSITION FOR POLISHING SEMICONDUCTOR WAFER EDGE, AND POLISHING MACHINING METHOD

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INVENTOR-INFORMATION:

NAME

COUNTRY

TANAKA, HIROAKI

YOSHIDA, AKITOSHI

OGAWA, YOSHIHISA

INOUE, YUSUKE

INT-CL (IPC): H01 L 21/304; B24 B 9/00; B24 B 37/00; C09 K 3/14

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a polishing composition for effectively and stably polishing and machining the edge of a semiconductor wafer that is made of a silicon wafer, a compound wafer, or the like.

SOLUTION: In the polishing composition for polishing a semiconductor wafer edge, an average primary particle diameter being calculated by full sphere conversion from a specific surface area being measured by the BET method ranges from 8 to 50 nm, an average secondary particle diameter B being measured by the laser scattering method using a micro track UPA ranges from 12 to 200 nm, a ratio B/A of the average primary particle diameter A to the average secondary particle diameter B ranges from 1.4 to 12, the concentration of a silicon oxide particle for entire solution is 2-30 wt.% in a colloidal solution, and also a buffering operation is achieved between pH 8-11 containing a buffering solution where a weak acid in that the logarithmic value of the inverse number of an acid dissociation constant at 25°C ranges from 8.0 to 12.5 and a strong base are combined.

L7: Entry 2 of 2

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TITLE: Polishing composition for polishing edge of semiconductor wafer and polishing method

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ABSTRACTED-PUB-NO: JP2001118815A

BASIC-ABSTRACT:

NOVELTY - A polishing composition contains a buffer solution and has a buffer action at a pH range of 8-11.

DETAILED DESCRIPTION - The buffer solution consists of a colloidal solution consisting of silicon oxide particles having the following: (a) mean primary particle diameter A calculated in sphericity equivalent from a specific surface area measured by the Brunauer-Emmette-Teller method: 8-50 nm; (b) mean secondary particle diameter B measured by the laser scattering method by microtrack UPA: 12-200 nm; (c) ratio of mean secondary particle diameter B to mean primary particle diameter A, B/A , = 1.4-12; (d) concentration of entire solution = 2-30 percent by weight. The buffer solution is formed by a combination of a weak acid having a logarithmic value of the reciprocal number of an acid dissociation constant at 25 degrees C of 8.0-12.5 and a strong base.

USE - The polishing composition is used for polishing the edge of the semiconductor wafer. The method polishes the edge of the semiconductor wafer.

ADVANTAGE - The composition has superior polishing force and its persistence and effectively stably polishes the edge of the semiconductor wafer.

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(71) 出願人 000107745

スピードファム株式会社

神奈川県綾瀬市早川2647

(72) 発明者 田中 弘明

神奈川県綾瀬市早川2647 スピードファ

ム・アイベック株式会社内

(72) 発明者 吉田 明利

神奈川県綾瀬市早川2647 スピードファ

ム・アイベック株式会社内

(74) 代理人 100089406

弁理士 田中 宏 (外1名)

最終頁に続く

(54) 【発明の名称】 半導体ウェーハエッジ研磨用研磨組成物及び研磨加工方法

(57) 【要約】

【目的】 シリコンウェーハあるいは化合物ウェーハ等よりなる半導体ウェーハのエッジ部分を効果的にかつ安定に研磨加工を行なう研磨用組成物を提供する。

【構成】 BET法により測定した比表面積より真球換算で算出した平均一次粒子径Aが8～50 nmであり、マイクロトラックUPAによるレーザー散乱法で測定した平均二次粒子径Bが12～200 nmの範囲にあり、かつ前記平均一次粒子径Aと平均二次粒子径Bの比B/Aが1.4から12の範囲にあって、更に溶液全体に対する酸化珪素粒子の濃度が2～30重量%であるコロイド溶液であり、ことにより、25℃における酸解離定数の逆数の対数値が8.0～12.5の弱酸および強塩基を組み合わせた緩衝溶液を含むpH8～11の間で緩衝作用を有することを特徴とする半導体ウェーハエッジ研磨用研磨組成物である。

【特許請求の範囲】

【請求項1】BET法により測定した比表面積より真球換算で算出した平均一次粒子径Aが8〜50nmであり、マイクロトラックUPAによるレーザー散乱法で測定した平均二次粒子径Bが12〜200nmの範囲にあり、かつ前記平均一次粒子径Aと平均二次粒子径Bの比B/Aが1.4から12の範囲にあって、更に溶液全体に対する濃度が2〜30重量%である酸化珪素粒子のコロイド溶液であり、かつ、25℃における酸解離定数の逆数の対数値が8.0〜12.5の弱酸および強塩基を組み合わせた緩衝溶液を含むことによって、pH8〜11の間で緩衝作用を有することを特徴とする半導体ウェーハエッジ研磨用研磨組成物。

【請求項2】25℃における導電率が、酸化珪素粒子1重量部あたり20ms/m以上であることを特徴とする請求項第1項に記載の半導体ウェーハエッジ研磨用研磨組成物。

【請求項3】弱酸を構成する陰イオンが炭酸イオン、炭酸水素イオンであり、かつ強塩基を構成する陽イオンがアルカリ金属イオン、コリンイオン、テトラメチルアンモニウムイオンまたはアンモニウムイオンのうち少なくとも一つであることを特徴とする請求項第1項ないし請求項第2項に記載の半導体ウェーハエッジ研磨用研磨組成物。

【請求項4】合成樹脂発泡体、合成皮革あるいは不織布等からなるポリッシングパッドを貼付した回転可能なドラムを有するエッジ研磨加工機に、被加工物である半導体ウェーハを載置押圧し、請求項第1項ないし請求項第3項のいずれかに記載の半導体ウェーハエッジ研磨用研磨組成物を供給しつつ、前記ドラム及び被加工物の双方あるいはその一方を回転して研磨することを特徴とする半導体ウェーハのエッジ研磨加工方法。

【発明の詳細な説明】

【0001】

【発明が属する技術分野】本発明は、シリコンウェーハあるいは化合物ウェーハ等よりなる半導体ウェーハのエッジ部分の研磨加工を行なうウェーハエッジ研磨用研磨組成物に関する。更に本発明は前記ウェーハエッジ研磨用研磨組成物を使用して半導体ウェーハのエッジ部分の鏡面加工を行なう方法に係る。

【0002】

【従来の技術】シリコン単結晶等半導体素子を原材料としたIC、LSIあるいは超LSI等の電子部品は、シリコンあるいはその他の化合物半導体の単結晶のインゴットを薄い円板状にスライスしたウェーハに多数の微細な電気回路を書き込み分割した小片状の半導体素子チップを基に製造されるものである。インゴットからスライスされたウェーハは、ラッピング、エッチング、更にはポリッシングという工程を経て、少なくともその片面が鏡面に仕上げられた鏡面ウェーハに加工される。ウェー

ハは、その後のデバイス工程にてその鏡面仕上げされた表面に微細な電気回路が形成されて行くのであるが、半導体素子チップに分割されるまではウェーハは最初の円板状の形状を保ったまま加工されるのであり、各加工の間には洗浄、乾燥、搬送等の工程が入る。その間ウェーハの外周側面エッジの形状が切り立ったままでかつ未加工の粗な状態の面であると、そこが各工程中に装置や他物体と接触し微小破壊が起こり微細粒子が発生したり、その粗な状態の面の中に汚染粒子を巻き込み、その後の工程でそれが散逸して精密加工を施した面を汚染し、製品の歩留まりや品質に大きな影響を与えたりすることが多い。これを防止するために、ウェーハ加工の初期段階でエッジ部分の面取り（ベベリング）を行ない更にその部分を鏡面仕上げ（エッジポリッシング）することが一般に行なわれている。

【0003】上述のエッジポリッシングは、一般的には回転可能なドラムの表面に、合成樹脂発泡体、合成皮革あるいは不織布等からなるポリッシングパッドを貼付した研磨加工機に、工作物であるベベリングを施したシリコンウェーハ等のエッジ部分を回転させつつ傾斜押圧し、コロイダルシリカを主成分とした研磨用組成物溶液を供給しつつ、エッジ部分の研磨加工を行なう方法で行われる。しかし、この際用いられる研磨用組成物はウェーハの表面ポリッシングに用いられるものと同等のものが用いられる。

【0004】研磨用組成物としては、アルカリ成分を含んだ溶液に微細なコロイド状酸化珪素微粒子を分散した溶液が一般的に使用される。この加工は、その前の工程までの、例えばダイヤモンド砥石を使用したり、あるいは硬質なアルミナ系砥粒を用いた所謂機械的な加工とは異なるものであって、その成分であるアルカリの化学的作用、具体的にはシリコンウェーハ等被加工物に対する浸食性を応用したものである。すなわち、アルカリの腐食性により、ウェーハ等被加工物表面に薄い軟質の浸蝕層が形成される。その薄層を微細なコロイド状酸化珪素粒子の機械的作用により除去してゆくことにより加工が進むのである。

【0005】このような加工においては、コロイダルシリカの形状は重要なファクターとなる。すなわち、被加工物表面はアルカリによって腐食され薄層が形成されてゆくのであるが、この薄層の除去速度はコロイダルシリカの形状によって大きく変化する。コロイダルシリカの粒子径を大きくすれば、除去速度は速くなるが、研磨面にスクラッチが発生しやすくなる。ゆえに、その粒子は適度なサイズを有し、容易に破壊したり、あるいは高次に凝集してゲル化するものであってはならない。すなわち、酸化珪素粒子はアルカリにより形成された浸蝕層を機械的作用により効果的に除去してゆくものである。従って、除去後の新しい研磨面に何らかの影響を与えるようなものであってはならないのである。

【0006】従来より様々な研磨組成物がウェーハ等の研磨剤として提案されている。たとえば、米国特許第3170273号公報では、シリカゾル及びシリカゲルが研磨剤として提案されている。さらに米国特許第3328141号公報では、該懸濁液のpHを10.5~12.5の範囲内にすることにより、研磨速度が増大する事が開示されている。米国特許第4169337号公報では、アミン類を研磨用組成物に添加することが開示されている。特開平2-158684号公報には、水、コロイダルシリカ、分子量10万以上の水溶性高分子、水溶性塩類からなる研磨用組成物が開示されている。更に特開平5-154760号公報では、水溶性アミンの一種であるヒペラジンを、シリカゾルまたはシリカゲルのシリカ基準にて、10~80重量%含む研磨用組成物を使用した研磨方法を開示している。

【0007】シリコンウェーハあるいは化合物ウェーハ等よりなる半導体ウェーハのエッジ部分の研磨加工と、シリコンウェーハあるいは化合物ウェーハ等の平面ポリッシング条件を比較すると、後者に比較し前者は、エッジ部分に接触するポリッシングパッドの時間が短いため、加工面にかかる圧力を高く、かつ加工面に対するポリッシングパッドの線速度も速くしてある。すなわち、平面ポリッシングに比べ、エッジ部分の研磨加工工程は大変過酷な条件であるといえる。半導体ウェーハのエッジ部分は1000番程度のベリング用砥石で研磨された状態で供給されるので、その面粗さは大変粗い。このような加工条件下において、従来の半導体ウェーハ等の平面ポリッシング用研磨用組成物を用いても十分な研磨速度と面粗さは得られない。

【0008】

【発明が解決しようとする課題】本発明者等は、前述の従来の研磨用組成物及び研磨方法が持つ問題点に鑑み、研磨用組成物溶液として、微細な酸化珪素の微粒子を含むコロイド、即ちコロイダルシリカの水溶液であって、平均一次径が8~50nm、平均二次粒子径が12~200nmであり、かつ平均一次粒子径と平均二次粒子径の比、平均二次粒子径/平均一次粒子径が1.4~12の間にある酸化珪素粒子を2~30重量%を含むコロイド溶液からなり、pHが8~11の間でpHを緩衝する作用を有する研磨用組成物を用いることにより、シリコンウェーハ等の半導体ウェーハのエッジ部分の鏡面研磨加工が効果的に行なえることを見出し、本発明を完成するに至ったものであり、その目的と成す所は、研磨速度が速く、かつ良好な面粗さが得られる半導体ウェーハのエッジ部分の鏡面研磨加工を行なうウェーハエッジ研磨用研磨組成物を提供することにある。さらに本発明の他の目的は、前述のウェーハエッジ研磨用研磨組成物を用いた、半導体ウェーハのエッジ部分の鏡面研磨方法を提供することにある。

【0009】

【課題を解決するための手段】上述の目的は、BET法により測定した比表面積より真球換算で算出した平均一次粒子径Aが8~50nmであり、マイクロトラックUPAによるレーザー散乱法で測定した平均二次粒子径Bが12~200nmの範囲にあり、かつ前記平均一次粒子径Aと平均二次粒子径Bの比B/Aが1.4から12の範囲にあって、更に溶液全体に対する濃度が2~30重量%である酸化珪素粒子のコロイド溶液であり、かつ、25℃における酸解離定数の逆数の対数値が8.0~12.5の弱酸および強塩基を組み合わせた緩衝溶液を含むことによって、pH8~11の間で緩衝作用を有することを特徴とする半導体ウェーハエッジ研磨用研磨組成物にて達成される。本発明にいう半導体ウェーハとは、シリコンウェーハ、化合物ウェーハで表面に被膜を施していない所謂ベアウェーハのほか、表面に二酸化珪素等の絶縁膜を形成したもの、あるいはポリシリコン等の半導体膜、更には銅薄膜等の金属導体膜を施したものを指す。

【0010】更に本発明の他の目的は、合成樹脂発泡体、合成皮革あるいは不織布等からなるポリッシングパッドを貼付した回転可能なドラムを有するエッジ研磨加工機に、被加工体である半導体ウェーハを載置押圧し、前述の半導体ウェーハエッジ研磨用研磨組成物を供給しつつ、前記ドラム及び被加工物の双方あるいはその一方を回転して研磨することを特徴とする半導体ウェーハのエッジ研磨加工方法にて達成される。

【0011】

【発明の実施の形態】本発明においては、半導体ウェーハエッジ研磨用研磨組成物中に含まれる研磨材をある特定の粒子径と分布を持った酸化珪素微粒子を使用し、更にその微粒子を含む母液をある特定のpH範囲で緩衝作用を有する緩衝液とすることを特徴とするものである。すなわち、酸化珪素微粒子の平均一次粒子径Aを8~50nmとし、その二次凝集をした平均二次粒子径Bを12~200nmの範囲までに抑制し、更にその一次粒子径Aと二次粒子径Bとの比率B/Aを1.4から12の範囲に置くことによって始めて優れたエッジ鏡面加工が行なわれるのである。かかるサイズの酸化珪素微粒子を含んだ溶液はコロイド状の溶液を形成する。

【0012】酸化珪素の微粒子は平均一次粒子径が8nmより小さいとコロイド溶液が凝集し易く研磨用組成物としての安定性が低下する。また、平均一次粒子径が、50nm以上の場合、研磨用組成物としての性能に影響はないが、二次凝集粒子を安定して製造することは難しい。平均一次粒子径Aと平均二次粒子径Bの比、B/Aが1.4以下の場合、二次凝集していない酸化珪素の微粒子と研磨速度の差はない。B/Aが1.2以上の場合、高次に凝集した酸化珪素の微粒子が生成して、スクラッチを生じやすくなる。平均二次粒子径は、200nm以下が望ましい。平均二次粒子径が、200nmを超える

と、粒子の沈降性が増加し好ましくない。酸化珪素の濃度は、実際の研磨加工時において2〜30重量%であることが望ましい。

【0013】本発明に使用されるコロイダルシリカは、水ガラスより脱イオン化して製造したもの、ヒュームドシリカを水等に分散させたもの、有機ケイ素化合物を加水分解して製造したもの等が使用できる。酸化珪素の微粒子の平均一次粒子径は、酸化珪素微粒子の乾燥物の比表面積より、真球換算を行うことにより算出した。比表面積はBET法により測定した。酸化珪素の微粒子の平均二次粒子径は、マイクロトラックUPA (HONWEL社) レーザ散乱式粒度分布測定装置を利用して測定を行なった。測定した体積平均粒子径を平均二次粒子径とした。

【0014】本発明においては、安定な研磨力を持続するためには、溶液全体のpHを8〜11の範囲に保つことが肝要である。pHが8以下であると研磨速度は著しく低下し実用の範囲からは外れる。また、pHが11以上になると、コロイダルシリカが凝集を始めるため研磨組成物の安定性が低下しこれも実用の範囲から外れる。そしてまた、このpHは摩擦、熱、外気との接触あるいは他の成分との混合等、考えられる外的条件により容易に変化するようなものであってはならない。従って、本発明においては研磨組成物溶液自体を、外的条件の変化に対してpH変化の幅が少ない、所謂緩衝作用の強い液とすることが必要である。緩衝溶液を形成するためには、25℃における酸解離定数(K_a)の逆数の対数値(pK_a)が8.0〜12.5の範囲にある弱酸および強塩基を組合わせて使用することが必要である。25℃における酸解離定数の逆数の対数値が8.0以下の場合、pHを上昇させるために、弱酸及び強塩基を大量に添加することが必要となるため好ましくない。25℃における酸解離定数の逆数の対数値が12.5より大きいとpHを8〜11の範囲で安定させる大きな緩衝作用を持つ緩衝溶液を形成することができない。

【0015】本発明の緩衝作用を有する研磨用組成物溶液の形成に使用する弱酸としては、炭酸($pK_a=6.35, 10.33$)、ホウ酸($pK_a=9.24$)、磷酸($pK_a=2.15, 7.20, 12.35$)類及び水溶性の有機酸等があげられ、またその混合物であってもかまわない。また、強塩基としては、アルカリ金属の水酸化物、四級アンモニウム、アンモニウムなどが使用できる。本発明で述べる緩衝溶液とは、上述の組合せで形成され、溶液の中で弱酸が価数の異なるイオンとして解離している状態または、解離状態と未解離状態が共存している溶液を示し、少量の酸または、塩基が混入してもpHの変化が少ないことが特徴である。

【0016】本発明においては、研磨用組成物溶液の導電率を高くすることにより、研磨加工速度を著しく向上することができる。導電率とは液中の電気の通り易さを

示す数値であり、単位長さあたりの電気抵抗値の逆数値である。本発明においては単位長さあたりの導電率の数値(micro-Siemens)を酸化珪素1重量%あたりに換算した数値で示す。本発明においては、25℃における導電率が20mS/m/1%-SiO₂以上であれば研磨加工速度の向上に対して好ましく、25mS/m/1%-SiO₂以上であれば更に好ましい。導電率を上昇させる方法としては、次の二方法がある。一つは緩衝溶液の濃度を高くする方法、もう一つは塩類を添加する方法である。緩衝溶液の濃度を高くするには、酸と塩基のモル比を変えずに濃度のみを高くすればよい。塩類を添加する方法に用いる塩類は、酸と塩基の組み合わせより構成されるが、酸としては、強酸、弱酸いずれであってもかまわず、硫酸および、有機酸が使用できその混合物でも良い。塩基としては、強塩基、弱塩基いずれであっても良く、アルカリ金属の水酸化物、水溶性の四級アンモニウムの水酸化物、水溶性アミンが使用できその混合物であってもかまわない。弱酸と強塩基、強酸と弱塩基、弱酸と弱塩基の組み合わせで添加する場合は、緩衝溶液のpHを変化させることがあるため、大量に添加することは望ましくない。前述の二方法を併用してもかまわない。

【0017】本発明の研磨用組成物の物性を改良するため、界面活性剤、分散剤、沈降防止剤などを併用することができる。界面活性剤、分散剤、沈降防止剤としては、水溶性の有機物、無機層状化合物などがあげられる。また、本発明の研磨用組成物は水溶液としているが、有機溶媒を添加してもかまわない。本発明の研磨用組成物は、研磨時にコロイダルシリカ及び、塩基と添加剤と水を混合して調製してもよい。また、一般的にはコロイダルシリカとして、15〜65%の高濃度の組成物を調製しておき、水あるいは、水と有機溶媒の混合物で希釈して使用することが多い。

【0018】エッジホリッシングの場合、一般的には回転可能なドラムの表面に、合成樹脂発泡体、合成皮革あるいは不織布等からなるポリッシングパッドを貼付した研磨加工機に、ワーク(被加工物)であるベベリングを施したシリコンウェーハ等のエッジ部分を回転させつつ傾斜押圧し、研磨用組成物溶液を供給しながら、エッジ部分の研磨加工を行なう方法で行われる。本発明に用いるエッジホリッシング用加工機とは、例えばスピードファム・アイベック社製E P-I V型エッジポリッシング装置に示されるようなものであり、表面にポリッシングパッドを貼付した回転可能なドラムと、ワークを把持し回転し任意の角度で傾斜させる把持部とからなり、該把持部に取り付けられたワークのエッジ部分を前記ドラムに押圧し、研磨用組成物の液を供給しながらワークとドラムの双方を回転せしめ、ワークのエッジ部分の鏡面研磨加工を行なう。即ち、回転しつつ少しずつ上昇あるいは下降して位置を変えてゆくドラムに、ワークを回転させな

から一定の角度で押しあて、研磨組成物の液を加工部分に滴下しながらポリッシングを行なう。本発明の研磨用組成物を用いた半導体ウェーハエッジの具体的研磨加工方法は以下に述べる実施例にて明らかにされよう。

【0019】

【実施例】次に実施例及び比較例をあげて本発明の半導体ウェーハエッジ研磨用組成物、およびそれを用いた研磨加工方法を具体的に説明するが、特にこれにより限定を行なうものではない。本発明に使用した半導体ウェーハエッジ研磨装置およびそれによる研磨条件は以下の通りである。

研磨装置：スピードファム・アイベック株式会社製、E P-200-V型

ドラム回転数：1800RPM

ドラム上下速度：0.8mm/sec

研磨布：SUBA400（ロデールニッタ社製）

研磨用組成物流量：600ml/分

加工時間：片面90秒ずつ計3分間

研磨組成物のpHはpHメーターを用いて測定した。測定にあたっては、pH6.86と9.18のpH標準溶液であらかじめpH電極の校正を行なった後測定した。導電率は導電率計にて測定した。また、研磨面の評価は、集光灯下で目視にてヘイズ及びピットの状態を観察した。また、研磨速度は、研磨前後のシリコンウェーハの重量差より求めた。研磨面の評価は、サーフコムプロファイラーM2000（チャップマン、インスツルメント社製）を使用してエッジ面の表面粗さを測定した。エッジポリッシュが不完全であることにより発生するスレ残りは、光学顕微鏡を用い、800倍の倍率で加工後のワーク全周を調べた。

【0020】実施例および比較例で用いた研磨用組成物*

水	実施例1	実施例2	実施例3	実施例4	実施例5
シリカ濃度(%)	5	10	15	5	5
一次粒子径A nm	17	17	17	18	18
二次粒子径B nm	28	28	28	190	190
B/A	1.65	1.65	1.65	10.6	10.6
添加剤					
TMA ₂ CO ₃	0.05	0.05	0.05	0.05	
K ₂ CO ₃	0.05	0.05	0.05	0.05	0.14
KHCO ₃	0.01	0.01	0.01	0.01	0.01
(※1) K ₂ SO ₄					0.072
物性					
pH	10.2	10.2	10.3	10.2	10.4
導電率 (※2)	27	26	26	27	65
結果					
研磨速度 mg/min	2.6	2.8	3.1	2.7	3.2
表面粗さ nm	25	19	20	20	20
スレ残り	なし	なし	なし	なし	なし

【0023】

※ ※【表2】

*は、平均一次粒子径17nm、平均二次粒子径28nmの試作品の酸化珪素微粒子、及び、平均一次粒子径18nm、平均二次粒子径180nmのヒュームドシリカのいずれかを用いた。これを実験用の研磨剤として、シリカ分として必要量分取し、攪拌しながら、表1～表5に示す種類と量の添加剤を所定量添加し、純水を加え濃度を調整して本発明の研磨用組成物とした。添加物のうち、炭酸テトラメチルアンモニウム、炭酸水素テトラメチルアンモニウム、炭酸カルシウム、炭酸水素カルシウム、炭酸ナトリウム及び炭酸水素ナトリウムは弱酸としての炭酸(pKa=10.33)と強塩基との組み合わせになる塩であり本発明の緩衝溶液である。また、硫酸カルシウム及びジエタノールアミンは、導電率を上げるための添加物である。上述の方法にて各々半導体ウェーハの研磨実験を行なった。実施例1では、表面に2μmのポリシリコン膜を付与した8インチのシリコンウェーハを使用した。

【0021】実施例1～10、比較例1～5

表面に2μmのポリシリコン膜を付与した8インチのシリコンウェーハをワークとし、表1～表3に示した研磨組成物を用いてエッジ部分の鏡面研磨加工試験を行なった。結果を表1～表3に併記する。なお、表中において使用する略号は次のものを示す。

TMA₂CO₃：炭酸テトラメチルアンモニウム

TMAHCO₃：炭酸水素テトラメチルアンモニウム

DEA：ジエタノールアミン

また、表中における単位は以下の通りである。

*1（添加剤濃度）：M/Kg-SiO₂

*2（導電率）：mS/m/1%-SiO₂

【0022】

【表1】

	水準	実施例6	実施例7	実施例8	実施例9	実施例10
砥粒	シリカ濃度(%)	5	5	5	5	5
	一次粒子径A nm	17	17	17	18	18
	二次粒子径B nm	28	28	28	190	190
	B/A	1.65	1.65	1.65	10.6	10.6
添加剤 (※1)	TMA ₂ CO ₃	0.07	0.1	0.1		0.1
	TMAHCO ₃			0.01		0.01
	K ₂ CO ₃	0.07	0.1			
	KHCO ₃	0.02	0.01			
	Na ₂ CO ₃				0.1	
	NaHCO ₃				0.02	
物性	pH	10.1	10.3	10.3	10.0	10.3
	導電率 (※2)	37	52	25	28	24
結果	研磨速度 mg/min	3.0	3.4	2.5	2.7	2.9
	表面粗さ nm	18	19	20	20	22
	スレ残り	なし	なし	なし	なし	なし

【0024】

* * 【表3】

	水準	比較例1	比較例2	比較例3	比較例4	比較例5
砥粒	シリカ濃度(%)	5	1	5	5	5
	一次粒子径A nm	18	18	40	17	17
	二次粒子径B nm	22	22	40	22	28
	B/A	1.22	1.22	1.00	1.29	1.67
添加剤 (※1)	TMA ₂ CO ₃	0.05	0.05			
	K ₂ CO ₃	0.05	0.05			
	KHCO ₃	0.01	0.01			
	DEA				0.1	0.1
物性	pH	10.2	10.1	10.0	10.0	10.0
	導電率 (※2)	28	28	7	14	14
結果	研磨速度 mg/min	1.4	0.5	0.7	1.5	1.6
	表面粗さ nm	89	450	620	90	95
	スレ残り	ビット発生	研削痕 ビット発生	研削痕 ビット発生	ビット発生	ビット発生

【0025】表1および表2の実施例に示す結果から明らかなようにB/Aが1.4~12の範囲内にあり、酸化珪素の濃度が2~30重量%であり、かつ25℃における酸解離定数の逆数の対数値が8.0~12.5の弱酸および強塩基を組み合わせた緩衝溶液を含むpH8~11の間で緩衝作用を有するようにした研磨用組成物で、表面に2μmのポリシリコン膜を付与した8インチのシリコンウエーハのエッジ部分の加工を行なった実験においては、研磨速度、表面粗さともに満足し得る結果が得られ、また、表面の品質にも重大な欠陥がなく良好であった。これに対し、表3の比較例に示すようにB/Aが本発明の範囲を逸脱したり、緩衝作用を持たない研磨用組成物を用いたりした場合、研磨速度が低くまた、※

※特に研磨が不十分であるため面粗さが向上せず、もとの粗い面が残っていてポリッシングされていないことは明らかである。また欠陥も顕著に現れるようになる。

【0026】実施例11~15、比較例6~10

エッジ部分を1000番のベベリング用砥石で加工した8インチのシリコンウエーハの表面に0.3μmの膜厚の低温熱酸化酸化珪素膜を施与したものをワークとして、前述の条件で、表4~表5に示した研磨組成物を用いてエッジ部分の鏡面研磨加工試験を行なった。結果を表4~表5に併記する。

【0027】

【表4】

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	水研	実施例11	実施例12	実施例13	実施例14	実施例15
砥粒	シリカ濃度(%)	15	10	20	15	15
	一次粒子径A nm	17	17	17	18	18
	二次粒子径B nm	28	28	28	190	190
	B/A	1.65	1.65	1.65	10.6	10.6
添加剤	TMA ₂ CO ₃	0.05	0.05	0.05	0.05	
	K ₂ CO ₃	0.05	0.05	0.05	0.05	0.14
	KHCO ₃	0.01	0.01	0.01	0.01	0.01
	(※1) K ₂ SO ₄					
物性	pH	10.2	10.3	10.3	10.2	10.4
	導電率 (※2)	26	26	25	25	35
結果	研磨速度 ng/min	0.51	0.59	0.83	0.68	0.74
	表面粗さ nm	27	23	21	31	26
	スレ残り	なし	なし	なし	なし	なし

【0028】

* * 【表5】

	水研	比較例6	比較例7	比較例8	比較例9	比較例10
砥粒	シリカ濃度(%)	10	1	20	15	10
	一次粒子径A nm	18	18	40	17	17
	二次粒子径B nm	22	22	40	22	28
	B/A	1.22	1.22	1.00	1.29	1.65
添加剤	TMA ₂ CO ₃	0.05	0.05			
	K ₂ CO ₃	0.05	0.05			
	KHCO ₃	0.01	0.01			
	(※1) DEA				0.1	0.1
物性	pH	10.2	10.1	10.0	10.0	10.0
	導電率 (※2)	26	28	6	11	13
結果	研磨速度 ng/min	0.25	0.05	0.28	0.32	0.25
	表面粗さ nm	1050	3200	730	820	1600
	スレ残り	ビット発生 酸化膜スレ残り	研削痕多 酸化膜スレ残り	ビット発生 酸化膜スレ残り	ビット発生 酸化膜スレ残り	ビット発生 酸化膜スレ残り

【0029】表4に示した実施例の結果から明らかな通り、本発明の範囲内にある研磨用組成物を用いた場合は、酸化膜付きのシリコンウェーハのエッジ研磨において良好な結果を示すが、表5の比較例に示すようにB/Aが本発明の範囲を逸脱したり、その他の条件が充足されていない研磨用組成物を用いた場合、高硬質の酸化膜に対する研磨力が低く、特に研磨が不十分であるため面粗さが向上せず、もとの粗い面が残っていてポリッシングがほとんど進んでいないことは明らかである。また欠陥も顕著に現れるようになる。特に、比較例10に示すように十分に凝集した酸化珪素を使用してもアミンを添加しただけでは十分な研磨速度は得られず、酸化膜※

※のスレ残りが観察された。

【0030】

【発明の効果】以上述べた通り、本発明による研磨用組成物を用いれば、シリコンウェーハ等のエッジ研磨において卓越した効果が得られることは明らかであり、特に酸化膜等を施与した難削性のシリコンウェーハに対しても良好な結果を得ることができる。本発明により、従来比較的対策が不十分であった、ウェーハのエッジ部分の鏡面研磨加工において優れた研磨力とその持続性をもった研磨用組成物が得られたものであり、関連業界に及ぼす効果は極めて大である。

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(72)発明者 小川 佳久
神奈川県綾瀬市早川2647 スピードファ
ム・アイベック株式会社内

(72)発明者 井上 裕介
神奈川県綾瀬市早川2647 スピードファ
ム・アイベック株式会社内
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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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CLAIMS

[Claim(s)]

[Claim 1] The first [an average of] particle diameter A computed by real ball conversion from the specific surface area measured with the BET adsorption method is 8-50nm. It is in the range whose second [an average of] particle diameter B measured by the laser scattering-about method by the micro truck UPA is 12-200nm. B/A is in the range of 1.4 to 12. and the ratio of said first [an average of] particle diameter A and second [an average of] particle diameter B -- Are the colloidal solution of the oxidation silicon particle whose concentration to the whole solution is 2 - 30 % of the weight, and furthermore, by including the buffer solution with which the opposite numeric value of the inverse number of the acid dissociation constant in 25 degrees C combined the weak acid and the strong base of 8.0-12.5 The abrasive compound for semiconductor wafer edge polish characterized by having buffer action between pH 8-11.

[Claim 2] The abrasive compound for semiconductor wafer edge polish given in the 1st term of a claim to which the conductivity in 25 degrees C is characterized by being 20. or more second/m per oxidation silicon particle 1 weight section.

[Claim 3] The abrasive compound for semiconductor wafer edge polish given in the 1st term of a claim thru/or the 2nd term of a claim characterized by for the anions which constitute weak acid being carbonate ion and bicarbonate, and the cation which constitutes a strong base being at least one of alkali-metal ion, choline ion, tetramethyl ammonium ion, or ammonium ion.

[Claim 4] The edge polish processing approach of the semiconductor wafer characterized by rotating and grinding said drum and the both sides of a workpiece, or one of these, carrying out the installation press of the semiconductor wafer which is a workpiece, and supplying the abrasive compound for semiconductor wafer edge polish of a publication at the edge polish processing machine which has the pivotable drum which stuck the polishing pad which consists of synthetic-resin foam, synthetic leather, or a nonwoven fabric to either the 1st term of a claim thru/or the 3rd term of a claim.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the abrasive compound for wafer edge polish which performs polish processing of the edge part of the semiconductor wafer which consists of a silicon wafer or a compound wafer. Furthermore, this invention relates to the approach of performing mirror plane processing of the edge part of a semiconductor wafer using said abrasive compound for wafer edge polish.

[0002]

[Description of the Prior Art] Electronic parts, such as IC and LSI which made the raw material semiconductor materials, such as a silicon single crystal, or a VLSI, are manufactured based on the semiconductor device chip of the shape of a wafer which wrote in and divided many detailed electrical circuits into the wafer which sliced the ingot of the single crystal of silicon or other compound semiconductors to disc-like [thin]. The wafer sliced from the ingot is further processed into the mirror plane wafer with which the mirror plane was made to the one side at least through wrapping, etching, and the process of polishing. Although a detailed electrical circuit is formed in the front face by which mirror plane finishing was carried out at a subsequent device process and a wafer goes, a wafer is processed with the first disc-like configuration maintained until it is divided into a semiconductor device chip, and, in between like each processing, processes, such as washing, desiccation, and conveyance, enter. while the configuration of the periphery side face edge of a wafer had rise steeply in the meantime, that contact equipment and other bodies into each process as it be the field of a raw **** condition, minute destruction take place, and a very fine particle occur, or the field which the contamination particle be involved in into the field of the **** condition, and it dissipated at the subsequent process, and performed precision processing be pollute, and it have big effect on the yield and the quality of a product in many cases. In order to prevent this, generally beveling an edge part by the initial stage of wafer processing (**** ring), and carrying out mirror plane finishing (edge polishing) of the part further is performed.

[0003] It is performed by the approach of performing polish processing of an edge part, above-mentioned edge polishing supplying the constituent solution for polish which carried out inclination press, making the polish processing machine which stuck the polishing pad which consists of synthetic resin foam, synthetic leather, or a nonwoven fabric rotate edge parts, such as a silicon wafer which gave the **** ring which is work, and used colloidal silica as the principal component to the front face of a pivotable drum generally. A deer is carried out and what has the constituent for polish equivalent to what is used for surface polishing of a wafer used in this case is used.

[0004] Generally as a constituent for polish, the solution which distributed the detailed colloid oxidation silicon particle is used for the solution containing an alkali component. This processing uses the diamond wheel to the process before that, or, unlike the so-called mechanical processing using a hard alumina system abrasive grain, applies a chemical operation of the alkali which is that component, and specifically as opposed to workpieces, such as silicon wafer's, erosion nature. That is, a thin elastic

erosion layer is formed in workpiece front faces, such as a wafer, of corrosive [of alkali]. Processing progresses by removing the thin layer by the mechanical work of a detailed colloid oxidation silicon particle.

[0005] In such processing, the configuration of colloidal silica serves as an important factor. That is, although a workpiece front face is corroded by alkali and a thin layer is formed, the removal rate of this thin layer changes with the configurations of colloidal silica a lot. Although a removal rate will become quick if the particle diameter of colloidal silica is enlarged, it becomes easy to generate a scratch in a polished surface. Therefore, the particle has moderate size, and it must not destroy easily, or it is condensed high order and it must not gel it. That is, an oxidation silicon particle removes effectively the erosion layer formed with alkali by the mechanical work. It seems "therefore, don't have a certain effect on the new polished surface after removal."

[0006] More various abrasive compounds than before are proposed as abrasive materials, such as a wafer. For example, in the U.S. Pat. No. 3170273 official report, a silica sol and silica gel are proposed as an abrasive material. Furthermore in the U.S. Pat. No. 3328141 official report, it is indicated by ****ing pH of this suspension within the limits of 10.5-12.5 that a polish rate increases. In the U.S. Pat. No. 4169337 official report, adding amines to the constituent for polish is indicated. Water, colloidal silica, the with a molecular weight of 100,000 or more water soluble polymer, and the constituent for polish that consists of water-soluble salts are indicated by JP,2-158684,A. Furthermore, in JP,5-154760,A, the polish approach which used the constituent for polish which contains the piperazine which is a kind of a water-soluble amine ten to 80% of the weight on the silica criteria of a silica sol or silica gel is indicated.

[0007] If flat-surface polishing conditions, such as a silicon wafer or a compound wafer, are compared with polish processing of the edge part of the semiconductor wafer which consists of a silicon wafer or a compound wafer, since the time amount of the polishing pad with which the former contacts an edge part is short as compared with the latter, in the pressure concerning a processing side, it is high and linear velocity of the polishing pad to a processing side has also been made quick. That is, compared with flat-surface polishing, it can be said that the polish processing process of an edge part is a severe condition very much. Since the edge part of a semiconductor wafer is supplied in the condition of having described about No. 1000 and having been ground with the grinding stone for ** rings, the field granularity is very coarse. Even if it uses constituents for polish for flat-surface polishing, such as the conventional semiconductor wafer, for the bottom of such a processing condition, sufficient polish rate and field granularity are not obtained.

[0008]

[Problem(s) to be Solved by the Invention] this invention person etc. takes an example by the trouble which the above-mentioned conventional constituent for polish and the above-mentioned conventional polish approach have. As a constituent solution for polish It is the water solution of the colloid containing the abrasive grain of detailed oxidation silicon, i.e., colloidal silica. The first [an average of] path is 8-50nm, and the second [an average of] particle diameter is 12-200nm. And the ratio of the first [an average of] particle diameter and the second [an average of] particle diameter, and the second [an average of] particle diameter / first [an average of] particle diameter consist the oxidation silicon particle between 1.4-12 of the colloidal solution containing 2 - 30 % of the weight. By using the constituent for polish which has the operation whose pH buffers pH between 8-11 The place which comes to complete a header and this invention and constitutes with the purpose that mirror-polishing processing of the edge part of semiconductor wafers, such as a silicon wafer, can be performed effectively A polish rate is to offer the abrasive compound for wafer edge polish which performs mirror-polishing processing of the edge part of the semiconductor wafer with which good field granularity is obtained quickly. Furthermore, other purposes of this invention are to offer the mirror-polishing approach of the edge part of a semiconductor wafer of having used the above-mentioned abrasive compound for wafer edge polish.

[0009]

[Means for Solving the Problem] The first [an average of] particle diameter A computed by real ball

conversion from the specific surface area which measured the above-mentioned purpose with the BET adsorption method is 8-50nm. It is in the range whose second [an average of] particle diameter B measured by the laser scattering-about method by the micro truck UPA is 12-200nm. B/A is in the range of 1.4 to 12. and the ratio of said first [an average of] particle diameter A and second [an average of] particle diameter B -- Are the colloidal solution of the oxidation silicon particle whose concentration to the whole solution is 2 - 30 % of the weight, and furthermore, by including the buffer solution with which the opposite numeric value of the inverse number of the acid dissociation constant in 25 degrees C combined the weak acid and the strong base of 8.0-12.5 It is attained by the abrasive compound for semiconductor wafer edge polish characterized by having buffer action between pH 8-11. With the semiconductor wafer said to this invention, semi-conductor film, such as a thing in which insulator layers, such as a silicon dioxide, were formed, or polish recon, and the thing which gave metallic conductor film, such as a copper thin film, further are also pointed out to a front face besides [which has not given the coat to a front face] the so-called bear wafer with a silicon wafer and a compound wafer. [0010] Furthermore, they are attained by the edge polish processing approach of the semiconductor wafer characterized by rotating and grinding said drum and the both sides of a workpiece, or one of these, other purposes of this invention carrying out the installation press of the semiconductor wafer which is a worked object, and supplying the above-mentioned abrasive compound for semiconductor wafer edge polish to the edge polish processing machine which has the pivotable drum which stuck the polishing pad which consists of synthetic-resin foam, synthetic leather, or a nonwoven fabric.

[0011]

[Embodiment of the Invention] In this invention, the oxidation silicon particle which had a certain specific particle diameter and distribution for the abrasives contained in the abrasive compound for semiconductor wafer edge polish is used, and it is characterized by using the mother liquor which contains the particle further as the buffer solution which has buffer action in a certain specific pH range. That is, the second [an average of] particle diameter B which set the first [an average of] particle diameter A of an oxidation silicon particle to 8-50nm, and carried out the secondary condensation is controlled even in the range of 12-200nm, and edge mirror plane processing which began and was excellent is performed by putting ratio B/A of the diameter A of a primary particle and diameter B of an aggregated particle on the range of 1.4 to 12 further. The solution containing the oxidation silicon particle of this size forms the solution of colloid.

[0012] If the particle of oxidation silicon has the first [an average of] particle diameter smaller than 8nm, the stability as a constituent for polish will fall that it is easy to condense the colloidal solution. Moreover, in the case of 50nm or more, there is no effect of the first [an average of] particle diameter in the engine performance as a constituent for polish, but it is difficult to be stabilized and to manufacture secondary floc. When the ratio of the first [an average of] particle diameter A and the second [an average of] particle diameter B and B/A are 1.4 or less, there are no particle of oxidation silicon and difference of a polish rate which are not condensed secondarily. When B/A is 12 or more, the particle of the oxidization silicon condensed high order generates, and it becomes easy to produce a scratch. The second [an average of] particle diameter has desirable 200nm or less. If the second [an average of] particle diameter exceeds 200nm, it increases [the sedimentation nature of a particle] and is not desirable. As for the concentration of oxidation silicon, it is desirable at the time of actual polish processing that it is 2 - 30 % of the weight.

[0013] What was deionized and manufactured from water glass, the thing which made water etc. distribute fumed silica, the thing which hydrolyzed and manufactured the organic silicon compound can be used for the colloidal silica used for this invention. The first [an average of] particle diameter of the particle of oxidation silicon was computed by performing real ball conversion from the specific surface area of the dry matter of an oxidation silicon particle. Specific surface area was measured with the BET adsorption method. The second [an average of] particle diameter of the particle of oxidation silicon measured using the micro truck UPA (HONEWELL) laser dispersion type particle-size-distribution measuring device. Measured volume mean particle diameter was made into the second [an average of] particle diameter.

[0014] In this invention, in order to maintain the stable polish force, it is important to maintain pH of the whole solution at the range of 8-11. A polish rate falls remarkably that pH is eight or less, and it separates from the range of practical use. Moreover, if pH becomes 11 or more, in order that colloidal silica may begin condensation, the stability of an abrasive compound will fall and it will separate also from this from the range of practical use. This pH seems and not to change with the external conditions considered, such as contact in friction, heat, and the open air, or mixing with other components, easily again. Therefore, it is required for the width of face of pH change to use the abrasive compound solution itself as the so-called strong liquid of little buffer action to change of external conditions in this invention. In order to form buffer solution, it is required for the opposite numeric value (electric dissociation exponent) of the inverse number of the acid dissociation constant (K_a) in 25 degrees C to use it combining the weak acid and the strong base in the range of 8.0-12.5. the inverse number of the acid dissociation constant in 25 degrees C -- a logarithm -- since it is necessary to add weak acid and a strong base in large quantities in order to raise pH, when a value is 8.0 or less, it is not desirable. the logarithm of the inverse number of the acid dissociation constant in 25 degrees C -- if a value is larger than 12.5, buffer solution with the big buffer action which stabilizes pH in 8-11 cannot be formed.

[0015] As weak acid used for formation of the constituent solution for polish which has the buffer action of this invention, carbonic acid (6.35 electric dissociation exponent= 10.33), a boric acid (electric dissociation exponent=9.24), phosphoric acid (7.20 electric dissociation exponent=2.15, 12.35), a water-soluble organic acid, etc. may be raised, and you may be the mixture. Moreover, as a strong base, the hydroxide of alkali metal, the fourth class ammonium, ammonium, etc. can be used. It is the description that the buffer solution stated by this invention has little change of pH even if it is formed in above-mentioned combination, the solution with which the condition which weak acid has dissociated in a solution as ion with which valences differ, or a dissociation condition and the condition of not dissociating lives together is shown and a small amount of acid or base mixes.

[0016] In this invention, polish working speed can be remarkably improved by making the conductivity of the constituent solution for polish high. Conductivity is a numeric value which shows easy as the electrical and electric equipment in liquid, and is the inverse number value of the electric resistance value per unit length. The numeric value which converted the numeric value (micro-Siemens) of the conductivity per unit length into per 1 % of the weight of oxidation silicon in this invention shows. In this invention, if the conductivity in 25 degrees C is two or more 20 mS/m / 1% - SiO(s), it is desirable to improvement in polish working speed, and if it is two or more 25 mS/m / 1% - SiO(s), it is still more desirable. There is the following two-way-type method as an approach of raising conductivity. The approach one makes concentration of buffer solution high, and another are the approaches of adding salts. What is necessary is to make only concentration high, without changing the mole ratio of an acid and a base, in order to make concentration of buffer solution high. although the salts used for the approach of adding salts consist of combination of an acid and a base -- as an acid -- strong acid and weak acid -- you may be any and the mixture is [a mineral acid and an organic acid can be used and] sufficient. as a base -- a strong base and a weak base -- you may be any, the hydroxide of alkali metal, the hydroxide of the water-soluble fourth class ammonium, and a water-soluble amine can be used, and it does not matter even if it is the mixture. Since pH of buffer solution may be changed when adding in the combination of weak acid, a strong base and strong acid, a weak base and weak acid, and a weak base, adding in large quantities is not desirable. The above-mentioned two-way-type method may be used together.

[0017] Since the physical properties of the constituent for polish of this invention are improved, a surfactant, a dispersant, a sedimentation inhibitor, etc. can be used together. As a surfactant, a dispersant, and a sedimentation inhibitor, the water-soluble organic substance, an inorganic stratified compound, etc. are raised. Moreover, an organic solvent may be added although the constituent for polish of this invention is used as the water solution. The constituent for polish of this invention may mix and prepare colloidal silica and a base and an additive, and water at the time of polish. Moreover, generally 15 - 65% of high-concentration constituent is prepared as colloidal silica, and it is diluted and used with the mixture of water or water, and an organic solvent in many cases.

[0018] It be carry out by the approach of perform polish processing of an edge part , carry out inclination press and supply the constituent solution for polish to it generally , in the case of edge polishing , make the polish processing machine which stuck the polishing pad which consist of synthetic resin foam , synthetic leather , or a nonwoven fabric rotate edge parts , such as a silicon wafer which gave the **** ring which be a work piece (workpiece) , on the front face of a pivotable drum . With the processing machine for edge polishing used for this invention for example, a speed femme -- with the pivotable drum which stuck the polishing pad on the front face, as shown in EP[by - eye peck company]-IV mold edge polish equipment Consist of the grasping section which grasps a work piece, rotates and is made to incline at an angle of arbitration, and press the edge part of the work piece attached in this grasping section to said drum, and the both sides of a work piece and a drum are made to rotate, supplying the liquid of the constituent for polish, and mirror-polishing processing of the edge part of a work piece is performed. That is, it presses at a fixed include angle, making the drum into which it goes up or descends little by little, and a location is changed, rotating rotate a work piece, and polishing is performed while the liquid of an abrasive compound is dropped at a processing part. The concrete polish processing approach of the semiconductor wafer edge using the constituent for polish of this invention will be clarified in the example described below.

[0019]

[Example] Next, although an example and the example of a comparison are given and the constituent for semiconductor wafer edge polish of this invention and the polish processing approach using it are explained concretely, this does not limit especially. The polish conditions by the semiconductor wafer edge polish equipment and it which were used for this invention are as follows.

Polish equipment: Speed femme eye peck incorporated company make, EP-200-V type drum rotation number:1800RPM drum normal velocity:0.8 mm/sec abrasive cloth:SUBA400 (Rodel Nitta CO. make) constituent flow rate for polish: -- a part for 600ml/-- floor-to-floor-time: -- it measured pH of an abrasive compound 90 seconds of one side at a time using the pH meter for a total of 3 minutes. In measurement, it measured, after proofreading a pH electrode beforehand with the pH standard solution of pH 6.86 and 9.18. Conductivity was measured with the conductivity meter. Moreover, evaluation of a polished surface observed the condition of a haze ** pit visually under the condensing LGT. Moreover, the polish rate was found from the weight difference of the silicon wafer before and behind polish. Evaluation of a polished surface measured the surface roughness of an edge side using the surfboard COM profiler M2000 (made in [instrument company] Chapman). The friction mark remainder which carries out **** generating investigated the work-piece perimeter after processing by one 800 times the scale factor of this using the optical microscope for an edge polish to be imperfect.

[0020] Either of the fumed silica with the oxidation silicon particle of a prototype with a particle diameter [first / an average of / of 17nm] and a particle diameter [second / an average of] of 28nm and a particle diameter [first / an average of / of 18nm], and a particle diameter [second / an average of] of 180nm was used for the constituent for polish used in the example and the example of a comparison. Having carried out initial-complement preparative isolation as a part for a silica, and agitating this as an abrasive material for an experiment, specified quantity addition of the additive of the class shown in Table 1 - 5 and an amount was carried out, and pure water was added, concentration was adjusted and it considered as the constituent for polish of this invention. Among additives, carbonic acid tetramethylammonium, carbonic acid hydrogen tetramethylammonium, a calcium carbonate, calcium hydrogencarbonate, a sodium carbonate, and a sodium hydrogencarbonate are salts which become the combination of the carbonic acid (electric dissociation exponent=10.33) as weak acid, and a strong base, and are buffer solution of this invention. Moreover, a calcium sulfate and diethanolamine are the additives for gathering conductivity. The polish experiment of a semiconductor wafer was respectively conducted by the above-mentioned approach. In the example 1, the 8 inches silicon wafer which gave the 2-micrometer polish recon film to the front face was used.

[0021] The 8 inches silicon wafer which gave the 2-micrometer polish recon film to one to examples 1-10 and example of comparison 5 front face was used as the work piece, and the mirror-polishing processing trial of an edge part was performed using the abrasive compound shown in Table 1 - 3. A

result is written together to Table 1 - 3. In addition, the cable address used in front Naka shows the following.

TMA -- 2CO₃:carbonic acid tetramethylammonium TMAHCO₃:carbonic acid hydrogen tetramethylammonium DEA: -- diethanolamine and the unit in front Naka are as follows.

* 1(additive concentration):M/kg-SiO₂*2(conductivity):mS/m/1%-SiO₂ [0022]

[Table 1]

	水準	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
砥粒	シリカ濃度 (%)	5	10	15	5	5
	一次粒子径 A nm	17	17	17	18	18
	二次粒子径 B nm	28	28	28	190	190
	B / A	1.65	1.65	1.65	10.6	10.6
添加剤	TMA ₂ CO ₃	0.05	0.05	0.05	0.05	
	K ₂ CO ₃	0.05	0.05	0.05	0.05	0.14
	KHCO ₃	0.01	0.01	0.01	0.01	0.01
	(*) K ₂ SO ₄					0.072
物性	pH	10.2	10.2	10.3	10.2	10.4
	導電率 (*2)	27	26	26	27	65
結果	研磨速度 mg/min	2.6	2.8	3.1	2.7	3.2
	表面粗さ nm	25	19	20	20	20
	スレ残り	なし	なし	なし	なし	なし

[0023]

[Table 2]

	水準	実施例 6	実施例 7	実施例 8	実施例 9	実施例 10
砥粒	シリカ濃度 (%)	5	5	5	5	5
	一次粒子径 A nm	17	17	17	18	18
	二次粒子径 B nm	28	28	28	190	190
	B / A	1.65	1.65	1.65	10.6	10.6
添加剤	TMA ₂ CO ₃	0.07	0.1	0.1		0.1
	TMAHCO ₃			0.01		0.01
	K ₂ CO ₃	0.07	0.1			
	KHCO ₃	0.02	0.01			
(*)	Na ₂ CO ₃				0.1	
	NaHCO ₃				0.02	
物性	pH	10.1	10.3	10.3	10.0	10.3
	導電率 (*2)	37	52	25	28	24
結果	研磨速度 mg/min	3.0	3.4	2.5	2.7	2.9
	表面粗さ nm	18	19	20	20	22
	スレ残り	なし	なし	なし	なし	なし

[0024]

[Table 3]

	水準	比較例 1	比較例 2	比較例 3	比較例 4	比較例 5
砥粒	シリカ濃度 (%)	5	1	5	5	5
	一次粒子径 A nm	1 8	1 8	4 0	1 7	1 7
	二次粒子径 B nm	2 2	2 2	4 0	2 2	2 8
	B / A	1 . 2 2	1 . 2 2	1 . 0 0	1 . 2 9	1 . 6 7
添加剤	TMA ₂ CO ₃	0 . 0 5	0 . 0 5			
	K ₂ CO ₃	0 . 0 5	0 . 0 5			
	KHCO ₃	0 . 0 1	0 . 0 1			
	(※1) DEA				0 . 1	0 . 1
物性	pH	1 0 . 2	1 0 . 1	1 0 . 0	1 0 . 0	1 0 . 0
	導電率 (※2)	2 8	2 8	7	1 4	1 4
結果	研磨速度 mg/min	1 . 4	0 . 5	0 . 7	1 . 5	1 . 6
	表面粗さ nm	8 9	4 5 0	6 2 0	9 0	9 5
	スレ残り	ビット発生	研削痕 ビット発生	研削痕 ビット発生	ビット発生	ビット発生

[0025] B/A is within the limits of 1.4-12 so that clearly from the result shown in the example of Table 1 and 2. the logarithm of the inverse number of an acid dissociation constant [in / the concentration of oxidation silicon is 2 - 30 % of the weight, and / 25 degrees C] -- a value with the constituent for polish it was made to have buffer action between pH 8-11 containing the buffer solution which combined the weak acid and the strong base of 8.0-12.5 It is [the result which may be satisfied with a front face of a polish rate and surface roughness in the experiment which processed the edge part of the 8 inches silicon wafer which gave the 2-micrometer polish recon film is obtained, and / no serious defect for surface quality] and was good. On the other hand, as shown in the example of a comparison of Table 3, when B/A deviates from the range of this invention or uses the constituent for polish without buffer action, it is clear that field granularity of a polish rate does not improve since low again especially polish is inadequate, the coarse field of a basis remains and polishing is not carried out. Moreover, a defect also comes to appear notably.

[0026] The mirror-polishing processing trial of an edge part was performed on condition that the above-mentioned using the abrasive compound shown in Table 4 - 5 by using as a work piece what gave the low-temperature thermal oxidation oxidation silicon film of 0.3-micrometer thickness on the front face of the 8 inches silicon wafer which described examples 11-15, the example 6 of a comparison - 10 edge parts of No. 1000, and was processed with the grinding stone for ** rings. A result is written together to Table 4 - 5.

[0027]

[Table 4]

	水準	実施例11	実施例12	実施例13	実施例14	実施例15
砥粒	シリカ濃度 (%)	15	10	20	15	15
	一次粒子径 A nm	17	17	17	18	18
	二次粒子径 B nm	28	28	28	190	190
	B / A	1.65	1.65	1.65	10.6	10.6
添加剤	TMA ₂ CO ₃	0.05	0.05	0.05	0.05	
	K ₂ CO ₃	0.05	0.05	0.05	0.05	0.14
	KHCO ₃	0.01	0.01	0.01	0.01	0.01
	(※1) K ₂ SO ₄					
物性	pH	10.2	10.3	10.3	10.2	10.4
	導電率 (※2)	26	26	25	25	35
結果	研磨速度 ng/min	0.51	0.59	0.83	0.68	0.74
	表面粗さ nm	27	23	21	31	26
	スレ残り	なし	なし	なし	なし	なし

[0028]

[Table 5]

	水準	比較例6	比較例7	比較例8	比較例9	比較例10
砥粒	シリカ濃度 (%)	10	1	20	15	10
	一次粒子径 A nm	18	18	40	17	17
	二次粒子径 B nm	22	22	40	22	28
	B / A	1.22	1.22	1.00	1.29	1.65
添加剤	TMA ₂ CO ₃	0.05	0.05			
	K ₂ CO ₃	0.05	0.05			
	KHCO ₃	0.01	0.01			
	(※1) DEA				0.1	0.1
物性	pH	10.2	10.1	10.0	10.0	10.0
	導電率 (※2)	26	28	6	11	13
結果	研磨速度 ng/min	0.25	0.05	0.28	0.32	0.25
	表面粗さ nm	1050	3200	730	820	1600
	スレ残り	ビット発生 酸化膜スレ 残り	研削痕多 酸化膜スレ 残り	ビット発生 酸化膜スレ 残り	ビット発生 酸化膜スレ 残り	ビット発生 酸化膜スレ 残り

[0029] Although a good result is shown in edge polish of a silicon wafer with an oxide film when the constituent for polish which is within the limits of this invention is used a passage clear from the result of the example shown in Table 4 When the constituent for polish with which B/A does not deviate from the range of this invention, or other conditions are not satisfied as shown in the example of a comparison of Table 5 is used, It is clear that the polish force of field granularity over a high hard oxide film did not improve since low again especially polish was inadequate, but the coarse field of a basis remains, and polishing is hardly progressing. Moreover, a defect also comes to appear notably. Especially polish rate sufficient by having just added the amine, even if it used the fully condensed oxidation silicon, as shown in the example 10 of a comparison was not obtained, but the friction mark remainder of an oxide film was observed.

[0030]

[Effect of the Invention] If the constituent for polish by this invention is used as stated above, it is clear that the effectiveness which stood high in edge polish of a silicon wafer etc. is acquired, and a good result can be obtained also to the difficult-to-cut silicon wafer which especially gave the oxide film etc. The effectiveness which the constituent for polish which had the polish force which was excellent in

mirror-polishing processing of the edge part of a wafer whose cure was former comparatively inadequate, and its durability by this invention is obtained, and is exerted on the related industry is size very much.

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TECHNICAL FIELD

[The technical field to which invention belongs] This invention relates to the abrasive compound for wafer edge polish which performs polish processing of the edge part of the semiconductor wafer which consists of a silicon wafer or a compound wafer. Furthermore, this invention relates to the approach of performing mirror plane processing of the edge part of a semiconductor wafer using said abrasive compound for wafer edge polish.

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PRIOR ART

[Description of the Prior Art] Electronic parts, such as IC and LSI which made the raw material semiconductor materials, such as a silicon single crystal, or a VLSI, are manufactured based on the semiconductor device chip of the shape of a wafer which wrote in and divided many detailed electrical circuits into the wafer which sliced the ingot of the single crystal of silicon or other compound semiconductors to disc-like [thin]. The wafer sliced from the ingot is further processed into the mirror plane wafer with which the mirror plane was made to the one side at least through wrapping, etching, and the process of polishing. Although a detailed electrical circuit is formed in the front face by which mirror plane finishing was carried out at a subsequent device process and a wafer goes, a wafer is processed with the first disc-like configuration maintained until it is divided into a semiconductor device chip, and, in between like each processing, processes, such as washing, desiccation, and conveyance, enter. while the configuration of the periphery side face edge of a wafer had rise steeply in the meantime , that contact equipment and other bodies into each process as it be the field of a raw **** condition , minute destruction take place , and a very fine particle occur , or the field which the contamination particle be involved in into the field of the **** condition , and it dissipated at the subsequent process , and performed precision processing be pollute , and it have big effect on the yield and the quality of a product in many cases . In order to prevent this, generally beveling an edge part by the initial stage of wafer processing (**** ring), and carrying out mirror plane finishing (edge polishing) of the part further is performed.

[0003] It is performed by the approach of performing polish processing of an edge part , above-mentioned edge polishing supplying the constituent solution for polish which carried out inclination press , making the polish processing machine which stuck the polishing pad which consists of synthetic resin foam , synthetic leather , or a nonwoven fabric rotate edge parts , such as a silicon wafer which gave the **** ring which is work , and used colloidal silica as the principal component to the front face of a pivotable drum generally . A deer is carried out and what has the constituent for polish equivalent to what is used for surface polishing of a wafer used in this case is used.

[0004] Generally as a constituent for polish, the solution which distributed the detailed colloid oxidation silicon particle is used for the solution containing an alkali component. This processing uses the diamond wheel to the process before that, or, unlike the so-called mechanical processing using a hard alumina system abrasive grain, applies a chemical operation of the alkali which is that component, and specifically as opposed to workpieces, such as silicon wafer's, erosion nature. That is, a thin elastic erosion layer is formed in workpiece front faces, such as a wafer, of corrosive [of alkali]. Processing progresses by removing the thin layer by the mechanical work of a detailed colloid oxidation silicon particle.

[0005] In such processing, the configuration of colloidal silica serves as an important factor. That is, although a workpiece front face is corroded by alkali and a thin layer is formed, the removal rate of this thin layer changes with the configurations of colloidal silica a lot. Although a removal rate will become quick if the particle diameter of colloidal silica is enlarged, it becomes easy to generate a scratch in a polished surface. Therefore, the particle has moderate size, and it must not destroy easily, or it is

condensed high order and it must not gel it. That is, an oxidation silicon particle removes effectively the erosion layer formed with alkali by the mechanical work. It seems "therefore, don't have a certain effect on the new polished surface after removal."

[0006] More various abrasive compounds than before are proposed as abrasive materials, such as a wafer. For example, in the U.S. Pat. No. 3170273 official report, a silica sol and silica gel are proposed as an abrasive material. Furthermore in the U.S. Pat. No. 3328141 official report, it is indicated by ****ing pH of this suspension within the limits of 10.5-12.5 that a polish rate increases. In the U.S. Pat. No. 4169337 official report, adding amines to the constituent for polish is indicated. Water, colloidal silica, the with a molecular weight of 100,000 or more water soluble polymer, and the constituent for polish that consists of water-soluble salts are indicated by JP,2-158684,A. Furthermore, in JP,5-154760,A, the polish approach which used the constituent for polish which contains the piperazine which is a kind of a water-soluble amine ten to 80% of the weight on the silica criteria of a silica sol or silica gel is indicated.

[0007] If flat-surface polishing conditions, such as a silicon wafer or a compound wafer, are compared with polish processing of the edge part of the semiconductor wafer which consists of a silicon wafer or a compound wafer, since the time amount of the polishing pad with which the former contacts an edge part is short as compared with the latter, in the pressure concerning a processing side, it is high and linear velocity of the polishing pad to a processing side has also been made quick. That is, compared with flat-surface polishing, it can be said that the polish processing process of an edge part is a severe condition very much. Since the edge part of a semiconductor wafer is supplied in the condition of having described about No. 1000 and having been ground with the grinding stone for ** rings, the field granularity is very coarse. Even if it uses constituents for polish for flat-surface polishing, such as the conventional semiconductor wafer, for the bottom of such a processing condition, sufficient polish rate and field granularity are not obtained.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] If the constituent for polish by this invention is used as stated above, it is clear that the effectiveness which stood high in edge polish of a silicon wafer etc. is acquired, and a good result can be obtained also to the difficult-to-cut silicon wafer which especially gave the oxide film etc. The effectiveness which the constituent for polish which had the polish force which was excellent in mirror-polishing processing of the edge part of a wafer whose cure was former comparatively inadequate, and its durability by this invention is obtained, and is exerted on the related industry is size very much.

[Translation done.]

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MEANS

[Means for Solving the Problem] The first [an average of] particle diameter A computed by real ball conversion from the specific surface area which measured the above-mentioned purpose with the BET adsorption method is 8-50nm. It is in the range whose second [an average of] particle diameter B measured by the laser scattering-about method by the micro truck UPA is 12-200nm. B/A is in the range of 1.4 to 12. and the ratio of said first [an average of] particle diameter A and second [an average of] particle diameter B -- Are the colloidal solution of the oxidation silicon particle whose concentration to the whole solution is 2 - 30 % of the weight, and furthermore, by including the buffer solution with which the opposite numeric value of the inverse number of the acid dissociation constant in 25 degrees C combined the weak acid and the strong base of 8.0-12.5 It is attained by the abrasive compound for semiconductor wafer edge polish characterized by having buffer action between pH 8-11. With the semiconductor wafer said to this invention, semi-conductor film, such as a thing in which insulator layers, such as a silicon dioxide, were formed, or polish recon, and the thing which gave metallic conductor film, such as a copper thin film, further are also pointed out to a front face besides [which has not given the coat to a front face] the so-called bear wafer with a silicon wafer and a compound wafer. [0010] Furthermore, they are attained by the edge polish processing approach of the semiconductor wafer characterized by rotating and grinding said drum and the both sides of a workpiece, or one of these, other purposes of this invention carrying out the installation press of the semiconductor wafer which is a worked object, and supplying the above-mentioned abrasive compound for semiconductor wafer edge polish to the edge polish processing machine which has the pivotable drum which stuck the polishing pad which consists of synthetic-resin foam, synthetic leather, or a nonwoven fabric.

[0011]

[Embodiment of the Invention] In this invention, the oxidation silicon particle which had a certain specific particle diameter and distribution for the abrasives contained in the abrasive compound for semiconductor wafer edge polish is used, and it is characterized by using the mother liquor which contains the particle further as the buffer solution which has buffer action in a certain specific pH range. That is, the second [an average of] particle diameter B which set the first [an average of] particle diameter A of an oxidation silicon particle to 8-50nm, and carried out the secondary condensation is controlled even in the range of 12-200nm, and edge mirror plane processing which began and was excellent is performed by putting ratio B/A of the diameter A of a primary particle and diameter B of an aggregated particle on the range of 1.4 to 12 further. The solution containing the oxidation silicon particle of this size forms the solution of colloid.

[0012] If the particle of oxidation silicon has the first [an average of] particle diameter smaller than 8nm, the stability as a constituent for polish will fall that it is easy to condense the colloidal solution. Moreover, in the case of 50nm or more, there is no effect of the first [an average of] particle diameter in the engine performance as a constituent for polish, but it is difficult to be stabilized and to manufacture secondary floc. When the ratio of the first [an average of] particle diameter A and the second [an average of] particle diameter B and B/A are 1.4 or less, there are no particle of oxidation silicon and difference of a polish rate which are not condensed secondarily. When B/A is 12 or more, the

particle of the oxidation silicon condensed high order generates, and it becomes easy to produce a scratch. The second [an average of] particle diameter has desirable 200nm or less. If the second [an average of] particle diameter exceeds 200nm, it increases [the sedimentation nature of a particle] and is not desirable. As for the concentration of oxidation silicon, it is desirable at the time of actual polish processing that it is 2 - 30 % of the weight.

[0013] What was deionized and manufactured from water glass, the thing which made water etc. distribute fumed silica, the thing which hydrolyzed and manufactured the organic silicon compound can be used for the colloidal silica used for this invention. The first [an average of] particle diameter of the particle of oxidation silicon was computed by performing real ball conversion from the specific surface area of the dry matter of an oxidation silicon particle. Specific surface area was measured with the BET adsorption method. The second [an average of] particle diameter of the particle of oxidation silicon measured using the micro truck UPA (HONEYWELL) laser dispersion type particle-size-distribution measuring device. Measured volume mean particle diameter was made into the second [an average of] particle diameter.

[0014] In this invention, in order to maintain the stable polish force, it is important to maintain pH of the whole solution at the range of 8-11. A polish rate falls remarkably that pH is eight or less, and it separates from the range of practical use. Moreover, if pH becomes 11 or more, in order that colloidal silica may begin condensation, the stability of an abrasive compound will fall and it will separate also from this from the range of practical use. This pH seems and not to change with the external conditions considered, such as contact in friction, heat, and the open air, or mixing with other components, easily again. Therefore, it is required for the width of face of pH change to use the abrasive compound solution itself as the so-called strong liquid of little buffer action to change of external conditions in this invention. In order to form buffer solution, it is required for the opposite numeric value (electric dissociation exponent) of the inverse number of the acid dissociation constant (K_a) in 25 degrees C to use it combining the weak acid and the strong base in the range of 8.0-12.5. the inverse number of the acid dissociation constant in 25 degrees C -- a logarithm -- since it is necessary to add weak acid and a strong base in large quantities in order to raise pH, when a value is 8.0 or less, it is not desirable. the logarithm of the inverse number of the acid dissociation constant in 25 degrees C -- if a value is larger than 12.5, buffer solution with the big buffer action which stabilizes pH in 8-11 cannot be formed.

[0015] As weak acid used for formation of the constituent solution for polish which has the buffer action of this invention, carbonic acid (6.35 electric dissociation exponent= 10.33), a boric acid (electric dissociation exponent=9.24), phosphoric acid (7.20 electric dissociation exponent=2.15, 12.35), a water-soluble organic acid, etc. may be raised, and you may be the mixture. Moreover, as a strong base, the hydroxide of alkali metal, the fourth class ammonium, ammonium, etc. can be used. It is the description that the buffer solution stated by this invention has little change of pH even if it is formed in above-mentioned combination, the solution with which the condition which weak acid has dissociated in a solution as ion with which valences differ, or a dissociation condition and the condition of not dissociating lives together is shown and a small amount of acid or base mixes.

[0016] In this invention, polish working speed can be remarkably improved by making the conductivity of the constituent solution for polish high. Conductivity is a numeric value which shows easy as the electrical and electric equipment in liquid, and is the inverse number value of the electric resistance value per unit length. The numeric value which converted the numeric value (micro-Siemens) of the conductivity per unit length into per 1 % of the weight of oxidation silicon in this invention shows. In this invention, if the conductivity in 25 degrees C is two or more 20 mS/m / 1% - SiO(s), it is desirable to improvement in polish working speed, and if it is two or more 25 mS/m / 1% - SiO(s), it is still more desirable. There is the following two-way-type method as an approach of raising conductivity. The approach one makes concentration of buffer solution high, and another are the approaches of adding salts. What is necessary is to make only concentration high, without changing the mole ratio of an acid and a base, in order to make concentration of buffer solution high. although the salts used for the approach of adding salts consist of combination of an acid and a base -- as an acid -- strong acid and weak acid -- you may be any and the mixture is [a mineral acid and an organic acid can be used and]

sufficient. as a base -- a strong base and a weak base -- you may be any, the hydroxide of alkali metal, the hydroxide of the water-soluble fourth class ammonium, and a water-soluble amine can be used, and it does not matter even if it is the mixture. Since pH of buffer solution may be changed when adding in the combination of weak acid, a strong base and strong acid, a weak base and weak acid, and a weak base, adding in large quantities is not desirable. The above-mentioned two-way-type method may be used together.

[0017] Since the physical properties of the constituent for polish of this invention are improved, a surfactant, a dispersant, a sedimentation inhibitor, etc. can be used together. As a surfactant, a dispersant, and a sedimentation inhibitor, the water-soluble organic substance, an inorganic stratified compound, etc. are raised. Moreover, an organic solvent may be added although the constituent for polish of this invention is used as the water solution. The constituent for polish of this invention may mix and prepare colloidal silica and a base and an additive, and water at the time of polish. Moreover, generally 15 - 65% of high-concentration constituent is prepared as colloidal silica, and it is diluted and used with the mixture of water or water, and an organic solvent in many cases.

[0018] It be carry out by the approach of perform polish processing of an edge part , carry out inclination press and supply the constituent solution for polish to it generally , in the case of edge polishing , make the polish processing machine which stuck the polishing pad which consist of synthetic resin foam , synthetic leather , or a nonwoven fabric rotate edge parts , such as a silicon wafer which gave the **** ring which be a work piece (workpiece) , on the front face of a pivotable drum . With the processing machine for edge polishing used for this invention for example, a speed femme -- with the pivotable drum which stuck the polishing pad on the front face, as shown in EP[by - eye peck company]-IV mold edge polish equipment Consist of the grasping section which grasps a work piece, rotates and is made to incline at an angle of arbitration, and press the edge part of the work piece attached in this grasping section to said drum, and the both sides of a work piece and a drum are made to rotate, supplying the liquid of the constituent for polish, and mirror-polishing processing of the edge part of a work piece is performed. That is, it presses at a fixed include angle, making the drum into which it goes up or descends little by little, and a location is changed, rotating rotate a work piece, and polishing is performed while the liquid of an abrasive compound is dropped at a processing part. The concrete polish processing approach of the semiconductor wafer edge using the constituent for polish of this invention will be clarified in the example described below.

[Translation done.]

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EXAMPLE

[Example] Next, although an example and the example of a comparison are given and the constituent for semiconductor wafer edge polish of this invention and the polish processing approach using it are explained concretely, this does not limit especially. The polish conditions by the semiconductor wafer edge polish equipment and it which were used for this invention are as follows.

Polish equipment: Speed femme eye peck incorporated company make, EP-200-V type drum rotation number:1800RPM drum normal velocity:0.8 mm/sec abrasive cloth:SUBA400 (Rodel Nitta CO. make) constituent flow rate for polish: -- a part for 600ml/-- floor-to-floor-time: -- it measured pH of an abrasive compound 90 seconds of one side at a time using the pH meter for a total of 3 minutes. In measurement, it measured, after proofreading a pH electrode beforehand with the pH standard solution of pH 6.86 and 9.18. Conductivity was measured with the conductivity meter. Moreover, evaluation of a polished surface observed the condition of a haze ** pit visually under the condensing LGT. Moreover, the polish rate was found from the weight difference of the silicon wafer before and behind polish. Evaluation of a polished surface measured the surface roughness of an edge side using the surfboard COM profiler M2000 (made in [instrument company] Chapman). The friction mark remainder which carries out **** generating investigated the work-piece perimeter after processing by one 800 times the scale factor of this using the optical microscope for an edge polish to be imperfect.

[0020] Either of the fumed silica with the oxidation silicon particle of a prototype with a particle diameter [first / an average of / of 17nm] and a particle diameter [second / an average of] of 28nm and a particle diameter [first / an average of / of 18nm], and a particle diameter [second / an average of] of 180nm was used for the constituent for polish used in the example and the example of a comparison. Having carried out initial-complement preparative isolation as a part for a silica, and agitating this as an abrasive material for an experiment, specified quantity addition of the additive of the class shown in Table 1 - 5 and an amount was carried out, and pure water was added, concentration was adjusted and it considered as the constituent for polish of this invention. Among additives, carbonic acid tetramethylammonium, carbonic acid hydrogen tetramethylammonium, a calcium carbonate, calcium hydrogencarbonate, a sodium carbonate, and a sodium hydrogencarbonate are salts which become the combination of the carbonic acid (electric dissociation exponent=10.33) as weak acid, and a strong base, and are buffer solution of this invention. Moreover, a calcium sulfate and diethanolamine are the additives for gathering conductivity. The polish experiment of a semiconductor wafer was respectively conducted by the above-mentioned approach. In the example 1, the 8 inches silicon wafer which gave the 2-micrometer polish recon film to the front face was used.

[0021] The 8 inches silicon wafer which gave the 2-micrometer polish recon film to one to examples 1-10 and example of comparison 5 front face was used as the work piece, and the mirror-polishing processing trial of an edge part was performed using the abrasive compound shown in Table 1 - 3. A result is written together to Table 1 - 3. In addition, the cable address used in front Naka shows the following.

TMA -- 2CO₃:carbonic acid tetramethylammonium TMAHCO₃:carbonic acid hydrogen tetramethylammonium DEA: -- diethanolamine and the unit in front Naka are as follows.

* 1(additive concentration):M/kg-SiO₂*2(conductivity):mS/m/1%-SiO₂ [0022]

[Table 1]

	水準	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
砥粒	シリカ濃度 (%)	5	10	15	5	5
	一次粒子径 A nm	17	17	17	18	18
	二次粒子径 B nm	28	28	28	190	190
	B / A	1.65	1.65	1.65	10.6	10.6
添加剤	TMA ₂ CO ₃	0.05	0.05	0.05	0.05	
	K ₂ CO ₃	0.05	0.05	0.05	0.05	0.14
	KHCO ₃	0.01	0.01	0.01	0.01	0.01
	(*) K ₂ SO ₄					0.072
物性	pH	10.2	10.2	10.3	10.2	10.4
	導電率 (*2)	27	26	26	27	65
結果	研磨速度 mg/min	2.6	2.8	3.1	2.7	3.2
	表面粗さ nm	25	19	20	20	20
	スレ残り	なし	なし	なし	なし	なし

[0023]

[Table 2]

	水準	実施例 6	実施例 7	実施例 8	実施例 9	実施例 10
砥粒	シリカ濃度 (%)	5	5	5	5	5
	一次粒子径 A nm	17	17	17	18	18
	二次粒子径 B nm	28	28	28	190	190
	B / A	1.65	1.65	1.65	10.6	10.6
添加剤	TMA ₂ CO ₃	0.07	0.1	0.1		0.1
	TMAHCO ₃			0.01		0.01
	K ₂ CO ₃	0.07	0.1			
	KHCO ₃	0.02	0.01			
(*)	Na ₂ CO ₃				0.1	
	NaHCO ₃				0.02	
物性	pH	10.1	10.3	10.3	10.0	10.3
	導電率 (*2)	37	52	25	28	24
結果	研磨速度 mg/min	3.0	3.4	2.5	2.7	2.9
	表面粗さ nm	18	19	20	20	22
	スレ残り	なし	なし	なし	なし	なし

[0024]

[Table 3]

	水準	比較例 1	比較例 2	比較例 3	比較例 4	比較例 5
砥粒	シリカ濃度 (%)	5	1	5	5	5
	一次粒子径 A nm	1 8	1 8	4 0	1 7	1 7
	二次粒子径 B nm	2 2	2 2	4 0	2 2	2 8
	B / A	1 . 2 2	1 . 2 2	1 . 0 0	1 . 2 9	1 . 6 7
添加剤	TMA ₂ CO ₃	0 . 0 5	0 . 0 5			
	K ₂ CO ₃	0 . 0 5	0 . 0 5			
	KHCO ₃	0 . 0 1	0 . 0 1			
	(※1) DEA				0 . 1	0 . 1
物性	pH	1 0 . 2	1 0 . 1	1 0 . 0	1 0 . 0	1 0 . 0
	導電率 (※2)	2 8	2 8	7	1 4	1 4
結果	研磨速度 mg/min	1 . 4	0 . 5	0 . 7	1 . 5	1 . 6
	表面粗さ nm	8 9	4 5 0	6 2 0	9 0	9 5
	スレ残り	ピット発生	研削痕 ピット発生	研削痕 ピット発生	ピット発生	ピット発生

[0025] B/A is within the limits of 1.4-12 so that clearly from the result shown in the example of Table 1 and 2. the logarithm of the inverse number of an acid dissociation constant [in / the concentration of oxidation silicon is 2 - 30 % of the weight, and / 25 degrees C] -- a value with the constituent for polish it was made to have buffer action between pH 8-11 containing the buffer solution which combined the weak acid and the strong base of 8.0-12.5 It is [the result which may be satisfied with a front face of a polish rate and surface roughness in the experiment which processed the edge part of the 8 inches silicon wafer which gave the 2-micrometer polish recon film is obtained, and / no serious defect for surface quality] and was good. On the other hand, as shown in the example of a comparison of Table 3, when B/A deviates from the range of this invention or uses the constituent for polish without buffer action, it is clear that field granularity of a polish rate does not improve since low again especially polish is inadequate, the coarse field of a basis remains and polishing is not carried out. Moreover, a defect also comes to appear notably.

[0026] The mirror-polishing processing trial of an edge part was performed on condition that the above-mentioned using the abrasive compound shown in Table 4 - 5 by using as a work piece what gave the low-temperature thermal oxidation oxidation silicon film of 0.3-micrometer thickness on the front face of the 8 inches silicon wafer which described examples 11-15, the example 6 of a comparison - 10 edge parts of No. 1000, and was processed with the grinding stone for ** rings. A result is written together to Table 4 - 5.

[0027]

[Table 4]

	水準	実施例11	実施例12	実施例13	実施例14	実施例15
砥粒	シリカ濃度(%)	15	10	20	15	15
	一次粒子径 A nm	17	17	17	18	18
	二次粒子径 B nm	28	28	28	190	190
	B/A	1.65	1.65	1.65	10.6	10.6
添加剤	TMA ₂ CO ₃	0.05	0.05	0.05	0.05	
	K ₂ CO ₃	0.05	0.05	0.05	0.05	0.14
	KHCO ₃	0.01	0.01	0.01	0.01	0.01
	(#1) K ₂ SO ₄					
物性	pH	10.2	10.3	10.3	10.2	10.4
	導電率 (#2)	26	26	25	25	35
結果	研磨速度 mg/min	0.51	0.59	0.83	0.68	0.74
	表面粗さ nm	27	23	21	31	26
	スレ残り	なし	なし	なし	なし	なし

[0028]

[Table 5]

	水準	比較例6	比較例7	比較例8	比較例9	比較例10
砥粒	シリカ濃度(%)	10	1	20	15	10
	一次粒子径 A nm	18	18	40	17	17
	二次粒子径 B nm	22	22	40	22	28
	B/A	1.22	1.22	1.00	1.29	1.65
添加剤	TMA ₂ CO ₃	0.05	0.05			
	K ₂ CO ₃	0.05	0.05			
	KHCO ₃	0.01	0.01			
	(#1) DEA				0.1	0.1
物性	pH	10.2	10.1	10.0	10.0	10.0
	導電率 (#2)	26	28	6	11	13
結果	研磨速度 mg/min	0.25	0.05	0.28	0.32	0.25
	表面粗さ nm	1050	3200	730	820	1600
	スレ残り	ビット発生 酸化膜スレ 残り	研削痕多 酸化膜スレ 残り	ビット発生 酸化膜スレ 残り	ビット発生 酸化膜スレ 残り	ビット発生 酸化膜スレ 残り

[0029] Although a good result is shown in edge polish of a silicon wafer with an oxide film when the constituent for polish which is within the limits of this invention is used a passage clear from the result of the example shown in Table 4 When the constituent for polish with which B/A does not deviate from the range of this invention, or other conditions are not satisfied as shown in the example of a comparison of Table 5 is used, It is clear that the polish force of field granularity over a high hard oxide film did not improve since low again especially polish was inadequate, but the coarse field of a basis remains, and polishing is hardly progressing. Moreover, a defect also comes to appear notably. Especially polish rate sufficient by having just added the amine, even if it used the fully condensed oxidation silicon, as shown in the example 10 of a comparison was not obtained, but the friction mark remainder of an oxide film was observed.

[Translation done.]